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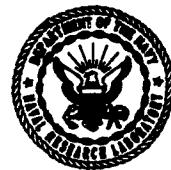
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Hexavalent Chromium: Toxicological Effects and Means for Removal from Aqueous Solution

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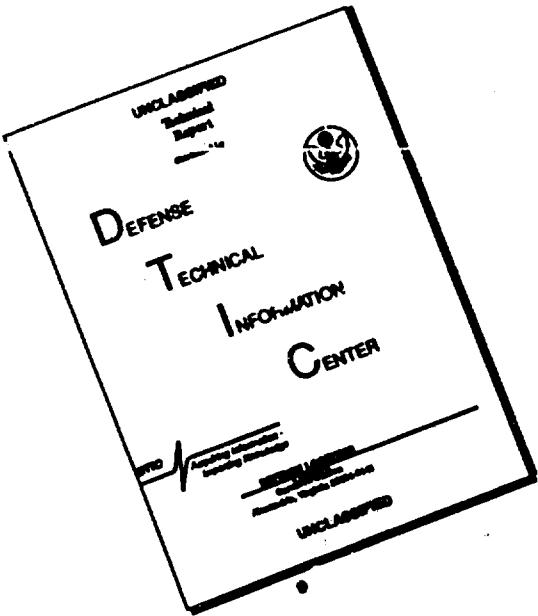


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ABSTRACT

There has been concern recently of the possibility of long-term disturbances of our environmental ecology by hexavalent chromium discharged in industrial and, in some cases, naval waste waters. To aid in the assessment of these potential dangers, the literature was surveyed to provide a perspective overview of the toxicities of hexavalent chromium toward plant and animal. The means available for reducing chromate concentrations in waste waters to ppm levels were reviewed for suitability for Navy usage. The techniques considered were chemical reduction, with subsequent precipitation of the trivalent chromium product; ion exchange; direct precipitation; ion flotation; electrochemical reduction; and electrodialysis.

Background and orientational information are furnished for use in considering Navy chromate pollution problems and their rectification.

PROBLEM STATUS

This is an interim report; work on the problem is continuing.

AUTHORIZATION

NRL Problem MO4-01
Project SF 51-542-601

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HEXAVALENT CHROMIUM: TOXICOLOGICAL EFFECTS AND MEANS FOR REMOVAL FROM AQUEOUS SOLUTION

INTRODUCTION

Chromium compounds have a wide range of industrial and commercial applications. One of the most important applications, and one of particular interest to the Navy, is in corrosion prevention and control, where the chromates are among the most effective corrosion inhibitors known. They can provide good protection for all common metals - iron, steel, brass, aluminum, and zinc - against corrosive attack in water over a wide range of pH and temperature. The chromates are generally effective against corrosion in galvanic couples produced by a bimetallic contact which tends to accelerate the corrosion of the more active metal. For particularly reactive couples, e.g., aluminum-copper, higher inhibitor concentrations are recommended for maximum protection, or the addition of a second synergistic inhibitor may be needed. The dissolved salts and gases, which occur commonly in water, are mostly nondeleterious, and most algicides and biocides are compatible with a chromate inhibition treatment. Chloride ion can cause pitting when the chromate concentration is low, but if sufficiently high dosages are maintained, the chromates can be inhibitive even in 25% refrigerator brines. Since the chromate effectiveness does not depend on the presence of oxygen, the chromates may be recommended for both open and closed systems.

Chromate is classed as an "anodic" inhibitor. Metallic corrosion in water occurs in two parts: an anodic reaction, $M \cdot M^{n+} + ne^-$, which ionizes the metal atom and separates it from the metallic phase, and a cathodic reaction, $R + ne^- \cdot R^n$, which serves to remove the residual electrons and maintain the electroneutrality of the corroding specimen. In low-temperature waters, the R species is usually hydronium ion in acidic solutions and dissolved oxygen in neutral and alkaline solutions. The overall corrosion reaction is diminished when either the anodic or cathodic partial reaction is inhibited. Anodic inhibitors, e.g., chromates, nitrates, orthophosphates, benzoates, molybdates, and tungstates, apparently promote the formation of a very protective, very thin film ($\gamma\text{-Fe}_2\text{O}_3$ in the case of iron and low-alloy steels) on the metal surface, which prevents easy removal of the ionized metal atom from the reaction site and effectively stifles the anodic reaction. Just how anodic inhibitors aid in the development of this "passivating" film remains uncertain, however, despite extended research on the subject. There are evidences that adsorption, either in conjunction with or after film formation, is a factor in the inhibitive action (1).

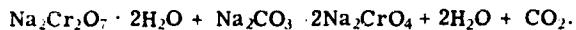
The dosages of chromate employed depend on the individual circumstances of the application. Current Navy practice, for example, specifies 700 to 1700 ppm sodium chromate at pH 8.25 to 9.75 for diesel engine coolant (2), 1700 ppm at pH 6.0 to 7.0 for radar cooling water (3), and 1700 ppm at pH 7.5 to 8.5 for locked-in ballast tank water (4). In commercial literature (5), the concentrations listed in Table 1 are recommended for the given systems.

Quite often smaller concentrations are used, especially when the following conditions are not present: high concentrations of aggressive ions (sulfate and chloride), strongly reactive galvanic couples, "external" reductants (e.g., hydrogen sulfide in the water),

Table 1
Recommended Chromate Concentrations
for Various Systems

System	(ppm) Sodium Chromate
Open recirculating water systems	250-500
Closed recirculating water systems, including automobiles and light diesels	500-1000
Marine engines	1000
Stationary diesels	500-1000
Power rectifiers	5000
Low-pressure boilers (100 psi) and hot- water heating systems	300-500
Refrigerator brines	10,000
Oil-well drilling mud	3000-5000

and unusual water temperatures and pH's. Since the bichromate is cheaper, the inhibitor is often added as sodium bichromate with this compound then being converted to the chromate by reaction with an alkali or carbonate:



It must be appreciated that although concentrations in the parts per million are being used, large quantities of material may in fact be involved. For example, one moderately sized cooling tower system (recirculation rate of 10,000 gpm, blowdown rate of approximately 100 gpm) operating at a chromate residual level of 30 to 35 ppm will discharge more than 7 tons of chromate annually (6). To dilute this amount of chromate to the 0.05 ppm standard established for potable water would require more than 30 billion gallons of water.

The chromates and chromium compounds can be toxic to plant and animal, and as our technology calls for ever-increasing tonnages of corrosion inhibitors, there has been concern regarding the wisdom of using chromium-containing materials for these purposes. Manifestations of chromate toxicity have been apparent over the years. Workers in chrome-plating plants commonly suffered nose membrane damage and "chrome holes," a characteristic penetrating ulcer occurring on the hands and forearms from contact with the plating solutions (7). A disproportionately high incidence of pulmonary carcinoma among employees of the chromate-producing industry was reported in the 1930's (8). In the fifties, lawsuits were filed by railroad employees who claimed to have contracted dermatitis from working with chromate inhibitors. These lawsuits led many railroads to adopt a nonchromate treatment for their diesel locomotive cooling systems (9).

Only relatively recently, however, has the toxicity of chromium compounds been investigated in low ppm concentrations, that is, when present essentially at pollutant levels. Results from a number of these investigations are reported below. The references do not represent a complete survey of the literature, and they relate, in the main, to experiments 5 to 10 years old or older. In the present era of concern over environmental pollution, new findings are sure to be forthcoming. Sufficient data have been collected thus far, however, to indicate clearly the deleterious effect in many instances of very small concentrations of chromium compounds. In reviewing the citations to follow, it should be borne in mind that toxicologic responses may differ depending on the type and degree of exposure, on environmental conditions, especially pH and oxygen availability, or simply because of differences in susceptibility among individuals and strains of a given species.

CHROMIUM TOXICITY TO WATER PLANTS AND ANIMALS

Chromium occurs in seawater at a concentration of 0.00005 ppm. No encompassing figure can be given for fresh water because of local variations. In one survey, the chromium content of 24 municipal water supplies was found to range from 0.001 to 0.04 ppm (10). Subsurface water from wells has been reported to contain up to 25 ppm of chromium (11). An enrichment factor is indicated in the metabolism of marine plants since they contain significantly more chromium (approximately 1 ppm) than the surrounding sea. The chromium content of marine animals generally falls between 0.2 and 1 ppm.

In the hexavalent form, chromium inhibits the growth of algae over a 0.03 to 0.4 ppm concentration range, depending on the species (12, 13). Smaller, sublethal chromium dosages sometime stimulate algae growth. Hexavalent chromium in seawater at 1 ppm reduced photosynthesis of the giant kelp *Macrocystis pyrifera* by 20 to 30 percent after 7 to 9 days; 5 ppm produced 50 percent inactivation of photosynthesis within 4 days (14, 15).

The efficiency of bacteria in sewage disposal plants is adversely affected by hexavalent chromium in concentrations as low as 1 to 2 ppm according to some authorities (16). After a 6-hour exposure to 1 ppm chromate solution, the respiration rate of a mass of bacteria remained unchanged, but only a small proportion could reproduce in ordinary media (17). Analogous tests with insect cells showed that the cell division process was hindered and that many of the affected cells suffered chromosome aberrations.

Among water animals, a considerable variation in tolerance to chromium exists, with the larger animals tending to be somewhat more resistant. *Daphnia* and *Microregma*, minute fresh-water crustaceans, show threshold effects at 0.016 to 0.7 ppm hexavalent chromium concentrations (18). The threshold of toxicity for the marine polychaete worm *Nereis virens* lies at about 1 ppm chromium, for the small prawn *Leander squilla*, about 5 ppm chromium, and for the shore crab *Carcinus maenas*, 10 ppm chromium (19).

A 2-year study of oyster mortalities in water containing 0.01 ppm chromium has indicated, however, that toxicologic effects may be cumulative even at these low concentrations (20). Nearly three-quarters of the oyster deaths occurred in the period May through July when physiological activity might be expected to be greatest, and it was postulated that as the contamination level of chromium increases, the ingestion-elimination balance is upset, causing extraordinary accumulation of the toxic metal.

Data concerning the toxicity of chromium toward a number of common fishes have been reported. In one of the earlier works, a limiting concentration of about 20 ppm hexavalent chromium was found for both rainbow trout and minnows (21). Later studies indicated a tolerance level of 45 ppm for blue gills exposed 20 days in hard water and of 200 ppm (using $K_2Cr_2O_7$) for mummichogs exposed in seawater for 1 week (22). Toxicity levels have been set by other workers for salmon (150 ppm) and rainbow trout (60 ppm) exposed to hexavalent chromium (23) and for bluegills exposed to chromium trioxide where 104 ppm was toxic in 6 to 84 hours (24). A recent study of the toxicity of several heavy metal salts to four species of warm-water fish showed, interestingly, that the trivalent chromium cation was significantly more toxic to each species than the hexavalent, the soft-water 96-hr TL* values ranging from 3 to 7 ppm for trivalent chromium and from 18 to 118 ppm for hexavalent chromium (25).

Little is known of chromium toxicity to the larger fish and warm-blooded water animals. Multitudinous varieties of smaller marine plant and animal life, each with

*The concentration of toxic material which kills 50% of the test animals in the stated time interval.

possibly a critical role in the ecological chain, remain untested. The toxicologic studies cited here, however, have served to set "no-go" limits; i.e., chromium concentration levels which, if exceeded, will, with considerable certainty, result in damage to the populations of known marine species. Further work can be expected only to lower these limits.

CHROMIUM TOXICITY TO LAND PLANTS AND ANIMALS

Although the disorders "yellow branch" in citrus plants and "witches broom" in tea are suspected to be due to excess chromium, chromium is regarded as generally innocuous as a trace element in the soil. The chromic and chromate ions have been found to be toxic in soil, however, and to adversely affect the more sensitive plants at concentrations as low as 5 ppm for each ion (26). Potassium dichromate and chromic chloride have been described as reducing the chlorophyll content, dry weight, and iron and manganese absorption of plants at minimum toxic levels of 18 mg chromium/cubic ft of soil for the dichromate and 180 mg chromium/cubic ft of soil for the chromic chloride (27).

Chromium toxicity to land animals may involve four types of exposure - contact with the intact epidermis, contact subcutaneously as in an open wound, inhalation, or ingestion.

Contact dermatitis can be induced, in some instances, by minimal exposure. Persons sensitive to chromium can develop allergic reactions merely from wearing chrome-plated watches and bracelets. Dermatitis has also resulted from handling chromium-containing cements (28) and lumber preserved by chromatic impregnation (29). Waters polluted by chromate bath wastes to only 7.8 ppm chromium have been reported recently as causing eczema among workers in Czechoslovakia (30). The hexavalent chromium ion might be expected to be the most eczemogenous agent in exposures of this type, for clinical tests have shown that while trivalent chromium is an irritant, the dematropic response to hexavalent chromium is ordinarily several orders of magnitude stronger (31). It should be noted also that the symptoms of mild chromate allergy are not confined to eczema but may include asthma, fever, nephritis, and the like (32).

Concentrated solutions of hexavalent chromium (chromic acid and its salts) are corrosive because of their extreme oxidizing potency, and in splash-type exposures they can produce wounds similar to acid burns. Exposures of a more extended nature, as the exposure of metal platers to the spray mists above highly concentrated chrome-plating baths, lead to penetrating ulcers at the point of mist contact, usually the hands and forearms, and to atrophy of the mucous membranes of the nose and often ulceration of the nasal septum as the mists are inhaled. The hand and forearm lesions are characteristically clean and nonsuppurative, although they are slow in healing and leave scars. The nasal passage ulcers, on the other hand, frequently exhibit purulent discharge and crusting; they often result in penetration of the nasal septum (33). Interestingly, one survey of the health of workers in the chromate industry disclosed that while over 50% of the personnel examined had active or healed chrome ulcers, only 2% gave evidence of contact dermatitis (34).

A further danger of skin contact with concentrated chromic solutions is the possibility of systematic poisoning by absorption through the skin. The chromate ion, for example, has been reported as being absorbed through the skin of rabbits in sufficient quantity to be systematically toxic (35). Fortunately, however, the occurrence of systematic illness as a result of chromium absorption is rare in the industry (36), although workers receiving splashes in the face have died as a result of the exposure (37). The death of one individual has been attributed to chromium poisoning caused by the use of a scabies ointment in which a chromate had been mistakenly substituted for sulfur (38).

Chromium is rapidly taken into the body system if chromic salts contact broken skin or open wounds, and severe poisoning can follow. Clinical reports exist of two attempts to cauterize wounds with chromic acid. In one instance, the patient died of acute nephritis (39). In the other, the patients, two women, survived with therapy, but suffered dizziness, headache, abdominal pain, and severe vomiting, the symptoms occurring within 20 minutes of the acid application (40).

Prolonged breathing of the dusts generated in chromate-extracting processes is accepted as a cause of lung cancer (34, 41). The disease is compensable in Germany for persons with a history of employment in the industry. Surveys in America have shown an incidence of lung cancer in chromate workers 29 times the norm for employees overall in the chemical industry (34).

The cancer-causing species has not been isolated, although analyses of the employment patterns of afflicted workers cast suspicion on the monochromate. Attempts to confirm this suspicion with laboratory animals, however, have either failed or been inconclusive (42). The carcinogenic action appears to be specific; skin and mucous membrane ulcers produced by chromate irritation do not become cancerous, nor is there undue incidence of gastrointestinal cancer although the involved workers must have also swallowed plant dust. In general, no correlation has been shown between external symptoms of chromate reaction, e.g., perforated septa, and lung cancer, and there is no clear evidence that plating employees, who may inhale the bath sprays, are unusually susceptible to carcinogenic attack.

Hexavalent chromium salts are poisonous and if ingested, may prove fatal with dosages as small as 5 to 10 g (43). Bulk ingestions of chromium compounds are rare, however. They, as all the chromate poisonings described thus far in this section, occur principally in the industrial realm where they are treatable by standard industrial hygiene practices of cleanliness, care in material handling, proper ventilation, and the use of respirators and protective clothing. On the other hand, the specter of continued pollution of our water sources by industrial discharges, many rich in hexavalent chromium, has raised health pathologists' concern as to the effects of an extended intake of low concentrations of the various chromium species as might happen in drinking polluted water.

Relevant data based on human experience are limited and most information has been gained with laboratory animals. One family is known to have drunk well water which ranged from 1 to 25 ppm chromate over a period of years without apparent effect (44). Conversely, there is the report of an unpublished experiment in which the subject, drinking water containing 10 ppm potassium dichromate, went for 3 weeks with only three periods of nausea, but subsequently became smitten with violent vomiting which caused the experiment to be terminated (45).

Toxicity studies with animals in which both trivalent and hexavalent chromium were added to their drinking water indicate that trivalent chromium is relatively harmless. Cats have been fed 1 g per day trivalent chromium as chromium phosphate without any apparent toxic effect (46). This parallels industrial hygiene experience where few if any work-related illnesses have been attributed to trivalent chromium salts.

Considerable tolerance is shown even to hexavalent chromium, it having been reported that potassium dichromate concentrations in drinking water as high as 500 ppm were not toxic to rats or rabbits (47). Rats given drinking water containing 1 to 25 ppm hexavalent chromium as potassium chromate survived a year without toxic symptoms (48). An examination of their bodies subsequent to this exposure revealed that below about 8 ppm, most chromium was eliminated, but above this level, appreciable quantities of chromium were retained in the various organs. Comparison with subjects fed

equivalent concentrations of the trivalent cation showed that hexavalent chromium was absorbed to a much greater extent than trivalent chromium. There was no evidence, however, of pathological deterioration in the affected organs in any of these experiments. Similar results were obtained with dogs fed up to 25 ppm hexavalent chromium for 4 years.

From the experiments just cited, chromium in low ppm concentrations is seemingly nondeleterious to mammals and may, in fact, even be beneficial, for rats receiving chromium had greater longevity than "control" rats who were fed no chromium. This was taken as possibly due to the role of chromium as a glucose tolerance factor (49). But on the other hand, there is a report of the induction of lung tumors in tumor-prone mice by 10 ppm potassium chromate in drinking water (17). Since the knowledge of chromate toxicity is limited and often contradictory, the USPHS has set the maximum permissible hexavalent chromium content in public drinking water at 0.05 ppm, the lowest concentration analytically determinable at the time the standards were established (44).

REMOVAL OF HEXAVALENT CHROMIUM FROM WATER

Under the Water Quality Act of 1965, hexavalent chromium may be present only in limited quantities in wastes discharged into public waterways since it is a potentially hazardous pollutant. The allowable concentrations are set by the individual states, but they are likely to be near the USPHS standard for potable water of 0.05 ppm, for waters discharged directly, and 5 ppm or less for waters turned into municipal sewage systems, because of the several detrimental effects of hexavalent chromium in sewage treatment (21).

Only a few means are available for achieving these low chromate levels; they include chemical reduction (with subsequent precipitation of the trivalent chromium product) and ion exchange, the two most used treatments presently, and largely unproved processes based on direct precipitation, ion flotation, electrochemical reduction, and electrodialysis.

Barium chromate is very sparingly soluble in neutral or alkaline water. In the past, principally in Europe (21, 50), barium chloride has been used to clear chromate-containing waters by precipitation of insoluble barium chromate. Barium chloride is expensive, however; an appropriate pH must be maintained; and care must be taken that unreacted barium chloride, which is highly poisonous and relatively soluble, is not carried over in the waste waters.

Some disadvantages of the barium treatment are overcome if precipitation is accomplished by mixing the waste stream with an agitated slurry of barium carbonate. Barium carbonate occurs naturally as the mineral witherite and is therefore relatively inexpensive. It has low solubility which alleviates the problem of barium carry-over but still dissolves from a slurry in sufficient quantity with time to precipitate the more insoluble barium chromate. Furthermore, as a carbonate, it tends to act as a buffer, holding the solution near a favorable 7.0 pH.

The witherite treatment has several shortcomings itself, however. Barium chromate has a solubility of about 4 ppm in 25°C water and to achieve 0.05 ppm or even 1 ppm hexavalent chromium requires a large excess of barium ion in solution. Also the precipitation and settling processes can be very slow, running into the tens of hours or even days, although these times can be shortened appreciably by the addition of a coagulating agent. A barium chromate-carbonate coagulant residue remains in the settling tanks to be periodically removed and disposed of by dumping (likely to be an increasingly

unpopular practice) or other means. In many instances, it would not represent a complete treatment because industrial wastes commonly contain undesirable species besides chromate to be removed, species such as copper and zinc cations, which are largely unaffected by witherite addition and require supplemental treatments for their removal.

Lead chromate is even less soluble than barium chromate, and an analogous treatment employing lead carbonate slurries appears possible, although none have been reported. Essentially the same problems of economy, toxicity, sludge removal, and incompleteness of treatment would likely be encountered.

Ion flotation has been suggested as a means of extracting chromium ion species from discharge waters. In ion flotation, an appropriate surfactant is added which reacts with the species to be removed from solution to form an insoluble surface-active compound. Being surface active, the new compound will segregate at the solution/air interface, and if a foam is generated, the compound will tend to concentrate in the foam phase because of its high solution/air interface area. Separation of the phases then serves to reduce the concentration of the original species remaining in the liquid phase. By use of relatively simple column and pumping systems, it is possible to perform all the operations above on a continuous basis and in series if desired, the depleted effluent from one column acting as feed for the next.

Laboratory tests have been made of the continuous ion flotation of dichromate using the cationic surfactant ethylhexadecyltrimethyl ammonium bromide, which showed the influence of several factors affecting the efficiency of the process (feed and withdrawal rates, dichromate to surfactant ratios, retention times, aeration rates, etc.) (51). Based on this work the prediction was made that a feed stream containing 100 ppm dichromate could be separated into effluent and collapsed foam streams containing 8 ppm and 468 ppm dichromate, respectively, by employing a three-column series operation with 400 ppm surfactant concentrations.

Although there is appeal in the prospect of removing chromates "on stream," no evidence was found in the literature of use of the continuous flotation method for chromate removal in actual waste water treatment. This particular application of ion flotation has been little studied, and improvements are likely possible, but at present there are several faults to be countered. For one, the predicted 8 ppm final dichromate level would not be adequate under many circumstances, and a fourth or even fifth stage treatment might be required. A stream rich in hexavalent chromium, and even more so in surfactant, is produced concurrently which, unless a use for it can be devised, must be treated itself, either for disposal or for reclamation of the original chromate and surfactant reagents. The possibilities of interference by surface oils, debris, foreign ions (which may exceed the chromate concentrations by 10 to 20 times), and excessively high or low pH need to be evaluated. And there is a question of the economic competitiveness of flotation with, for example, ion exchange, especially if the chromate and surfactant reagents cannot be reclaimed cheaply.

Electrochemical oxidation or reduction has been proposed in the past for certain discharge water contaminants, e.g., the oxidation of cyanide wastes to cyanates (52), but the technique has not been extensively applied, perhaps partly because of the necessity of using concentrated solutions to achieve reasonable efficiency. Dilute solutions give high resistances and slow reaction rates because the ions must migrate through the solution to the electrodes before reaction can occur.

An electrolytic unit has been developed recently, however, which is claimed to eliminate the traditional disadvantages of electrolysis (53). The unit employs a bed of semiconductive material between the cathode and anode. Current flows through the bed

itself, and its conductivity is sufficiently high that an adequate current can be maintained with low voltages even when dilute, high-resistance solutions are passed through the unit. Also when voltage is applied, the individual granules of the bed polarize, each granule exhibiting anode and cathode regions where solution species may be either oxidized or reduced. The distance any ion must travel to find a reaction site is thus reduced greatly, and reaction times are claimed to be exceedingly fast.

The manufacturers have recommended this unit for the removal of chromate from cooling tower blowdown waters, the chromate being reduced electrochemically to trivalent chromium, which is precipitated after leaving the cell by a pH adjustment. Presumably it could be used for other waste waters having a low chromate concentration. The cell is new and essentially untested, however, and a number of operating factors, such as efficiency, capacity, response to foreign ions, and bed life, need impartial evaluation based on actual field experience. A sludge, albeit a relatively pure one, is left for retreatment or disposal.

Electrodialysis is used to produce potable water from brackish sources at rates of 100,000 to 1,000,000 gallons or even more per day. Proposals and studies have been made concerning the application of this technique to waste water purification (52, 54). For a deconcentrating operation, the elemental electrodialysis cell consists of three compartments, with the middle compartment separated from the cathode compartment by an ionic membrane permeable to cations, but not anions, and from the anode compartment by one permeable to anions, but not cations. The water to be treated is introduced into all three compartments. When voltage is applied, anions migrate to the anode, cations to the cathode, and the central compartment is depleted. If a "stack" of compartments formed by alternating cation- and anion-permeable membranes is placed between cathode and anode, the feed solution will be alternately enriched or depleted from one compartment to the next. Most units employ stacked compartments for increased efficiency. It is also possible to treat by stages, the effluent from one stage being taken as feed water for the next.

Ideally, electrodialysis would offer advantages for the removal of chromates. The ionic membranes do not become exhausted or require regeneration and the operation could be made continuous and essentially automatic. The output is chromate-free discharge water plus a concentrated solution of pure chromate salt ready for direct reuse, e.g., in cooling tower water, without further treatment.

In practice, however, electrodialysis has been found inefficient when final concentrations below 100 ppm are sought. In one study of the decontamination of reactor cooling water by electrodialysis, a unit consisting of 150 elementary cells with a membrane area of 1 square meter was required to effectively treat 100 cubic meter of effluent waters per day (55). A combination of electrodialysis and ion exchange in a single unit has been suggested as perhaps the most economic means of producing waters with very low impurity levels (54), especially since this arrangement would allow electrical regeneration of the ion exchange resin. On the other hand, waste waters containing 4000 ppm chromium trioxide have been reported as being reduced to 3 to 5 ppm chromium trioxide by three-stage electrodialysis (56).

Membrane capabilities are presently the limiting factor in electrodialysis; with the development of improved membranes (and possibly more sophisticated cell structures), the economical reduction of trace impurities to a few ppm concentration by direct electrodialysis is anticipated. There is no evidence, however, that this stage has yet been reached.

The oldest and by far most used method for clearing chromates from industrial waste waters is chemical reduction followed by precipitation. Commonly, the wastes

are acidified to pH 3 (reduction is slow at high pH), the chromates reduced by addition of a suitable agent, and the pH raised by introduction of an alkali, usually lime, to precipitate trivalent chromium and cations of other heavy metals which may be present, e.g., copper, zinc, iron, and nickel, as insoluble by hydroxides (less than 1 ppm in most cases) (52, 57). A number of readily available chemicals may serve as the reductant, including metallic iron and zinc, brass, sulfur dioxide, sodium sulfite, sodium bisulfite, zinc hydrosulfite, and sodium, or other, sulfides. The choice is based on economics and convenience in each individual application. In many instances, another by-product of the industrial plant (ferrous sulfate, flue gases) is used. The process may be carried out on a continuous or batch basis, and several companies* offer either complete systems or controlling mechanisms to allow automation of the various operations.

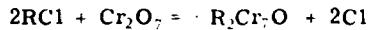
A major difficulty with this treatment lies in the removal and ultimately the disposal of the precipitated hydroxides. Metal hydroxides tend to be highly hydrated and voluminous when first formed; chromium hydroxide, in particular, may contain 75 to 80% water by volume. Consequently the precipitates are slow to settle and hard to separate from the water phase. To hasten the process, coprecipitators and coagulating agents are often used, as well as mechanical flocculators. Because of the slowness of the precipitate in settling, it is usually necessary to hold the treated water in settling tanks or basins until it clears. The purified water is then discharged and the sediment sludge filter dried or, more often, pumped out onto beds or into lagoons for final drying. The value of the metals contained in the sludge is seldom sufficient to justify an attempt at reclamation and in the past accumulated dry sludge was disposed of in sinkholes, abandoned mine shafts, the ocean, or as land fill. As population and pollution increase, however, acceptable depositories may be expected to become more difficult to find.

When ion exchange is used for chromate removal, the sludge problem is avoided, and the chemical is returned in a state fit for direct reuse in many applications. This advantage was appreciated for many years, but only in the last 10 to 15 years have ion exchange resins capable of withstanding the oxidizing powers of chromate been available to make the process feasible in the field. The technique was first used in the plating industry, where the waste volumes are relatively small, the concentrations are high, and the value of the chromates, which would otherwise be lost in discharge, is a considerable part of the operating expense. Pollution restrictions are now acting, along with improved ion exchange technology, to extend ion exchange into the field of cooling tower blowdown water treatment, where volumes in the millions of gallons at 10 to 300 ppm chromate are involved.

For the removal of chromates from cooling tower discharge water, a strong base ion resin is used, e.g., Nalcite SBR or Rohm and Haas IRA-400, usually in the chloride form. If used in the base form, the eluted hydroxyl ions would react with heavy metal cations in the stream to give clogging metal hydroxide precipitates. The exchange reaction in neutral water (6) may be considered as

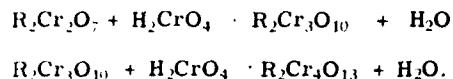


If the discharge stream is acidified, however, the dichromate becomes the prevalent species and the reaction is



*Hytek-International, Hytek Park, 13721 Bennington Ave., Cleveland, Ohio; Sethco Controls, Inc., One Bennington Ave., Freeport, N.Y.; Graver Water Conditioning Co., U.S. Highway 22, Union N.J.; and Schore Automations, Inc., 73 Rushmore St., Westbury, N.Y.

and depending on the concentration of the chromate and the acidity, polychromate adsorbates may be formed:



It can be seen that acidifying the chromate solution has the effect of doubling (or more) the capacity of the ion resin. The preferential retention of chromate species over sulfates, chlorides, and other competing anions has also been found to be enhanced as the pH is lowered. For these reasons, it is advantageous to adjust the pH of the water to 4.5 to 5.0 prior to chromate removal by ion exchange.

The efficiency of chromate removal from low concentration waters by ion exchange also depends on the flow rate through the resin bed. With the present resins (even using pH 5 waters), flow rates below 2 gallons per minute per cubic foot of resin are necessary if adequate resin capacities are to be obtained while "leakage" is limited at under 1 ppm (6).

Exhausted resins are regenerated most efficiently by elution first with sodium hydroxide-sodium chloride solution and then with sodium chloride solution alone. The sodium hydroxide converts the acid chromate back to the neutral chromate which is less strongly adsorbed and therefore more easily displaced by the chloride anion. The final sodium chloride wash removes residual chromate and excess hydroxyl ion.

To illustrate, in one test (6), simulated cooling tower blowdown water at pH 4.5 was passed through a strong base anion resin until the resin's exchange capacity was exhausted and "breakthrough" occurred. The resin was loaded to 7.7 pounds chromate per cubic foot at this point. The primary sodium hydroxide-sodium chloride regenerative treatment (2.5 pounds sodium hydroxide and 5.0 pounds sodium chloride per cubic foot of resin administered as a 10% brine solution) gave an effluent which contained chromate equivalent to 6.9 pounds per cubic foot of resin. The second dosage (5 pounds sodium chloride per cubic foot as 10% brine) liberated another 0.75 pounds per cubic foot which brought total recovery to 7.65 pounds per cubic foot, or 99.7% of the original chromate content of the resin. The collected effluent volume per cubic foot of resin was 6.5 gallons, the chromate thus being recovered at a concentration in excess of 10% by weight. The effluent is not completely free of impurities, since both sulfate ions (absorbed with the chromate during the exhaustion step) and chloride ions (from exhaustion or excess regenerant) are present at 1.60 and 0.80 pounds per cubic foot resin, respectively, but the chromate content is sufficiently in excess that, in most cooling water systems, the effluent can be used directly as a makeup reagent without harm.

Descriptions of pilot plant and on-stream operating experiences with ion exchange chromate recovery systems have been given (58), and comparisons of the economies of ion exchange versus chemical reduction-precipitation as a means of freeing waste streams from chromates have been made (59,60). The cost of chemicals (not counting resin replacement) for the recovery of a pound of chromate (\$0.04-\$0.05) is substantially less than the cost of replacing a pound of chromate (\$0.17-\$0.19), and, although a sizeable capital investment is required, it is considered that ion exchange becomes economically advantageous when blowdown rates greater than 100 gpm are to be treated. Complete, pre-engineered and installed ion exchange chromate recovery systems for cooling tower waters are available from several companies*.

*Cochrane Division, Crane Company, King of Prussia, Pa., and Nalco Chemical Co., 180 N. Michigan Ave., Chicago, Ill.

Ion exchange has its disadvantages also, however. For many applications, particularly when the adsorbate concentrations are low, the process may be unsatisfactory because it can be flow dominated. That is, there is a critical flow rate (usually in the neighborhood of 1 to 3 gallons per minute per cubic foot of resin) which, if exceeded even temporarily, results in incomplete exchange and the passage of chromate through the column, even though the column's capacity is still far from exhausted. Ion exchange is not likely to be useable therefore when large quantities of chromate-treated waters are discharged at high rates as in pumping of ships' ballast tanks. Moderate size flows can be handled, however, one system being offered for the treatment of a continuous 200 gpm blowdown stream from cooling towers which fits into a space 50 feet long by 15 feet wide by 15 feet high (61).

Other problems, not inherently limiting, include the maintenance of an adequate selectivity of the resin for chromate over foreign anions which may be introduced into the system, and the prevention of fouling of the resin bed by oils, wood degradation products, and other organics, or its clogging by debris or precipitated water hardness and metal hydroxides. The latter possibility is avoided by suitable filtering, and the first difficulty may be expected to be relatively rare, since it has been shown that chromate is preferentially adsorbed at pH 4.5 to 5.0 over phosphate, sulphate, and chloride ions, which are the anions most likely to be present in quantity.

CHROMATE POLLUTION AND THE NAVY

As a user of large quantities of chromates and other chromium-containing compounds, the Navy has an obligation to do all in its power to alleviate chromium pollution, both in coastal waters and on the high sea. Hexavalent chromium is stable in aerated water and may persist in locally high concentrations, when dumped in harbors or calm seas, for periods sufficient to damage indigenous marine populations. Although hexavalent chromium in the sea is ultimately reduced to trivalent chromium, there is substantial evidence (25, 62) that chromium in this ionic state is as toxic, if not more so, to ocean flora and fauna as the original hexavalent chromium species itself. The idea that trivalent chromium is innocuous because it hydrolyzes in neutral waters with the formation of insoluble hydrated oxides must be tempered with the knowledge that these oxides may be solubilized by local acidity (e.g., in fishes' stomachs after being ingested in the colloidal state) or by formation of soluble complexes (e.g., $\text{Cr}(\text{C}_2\text{O}_4)_3^{4-}$) or soluble organometallic compounds (cf., the role of methyl mercury in mercury poisoning from "insoluble" industrial mercury wastes (63)). Even when dumping-site damages are not detected, chromate discharges may cause the chromium concentrations in contained water bodies, such as lakes, bays, and harbors (if not the ocean itself), to reach levels where long-term poisonings of sensitive organisms, e.g., oysters (20), can occur with potential hazard to public economy and health.

Corrosion inhibitors provide savings of millions of dollars per year through reduced corrosion damage and downtime, and they contribute significantly to the Navy's tactical efficiency by prolonging the service life of vital shipboard components. The Navy cannot abandon their use. Abatement of chromate pollution by the Navy is possible, however, by (a) employment of nonchromate inhibitors where feasible and (b) an expansion of the Navy's use of chromate-removing treatments for waste waters from those applications where chromate-based inhibitors are essential.

Wider use of the latest methods in chromate-removal technology would reduce the Navy's contribution to chromate pollution of the environment. Large cooling water systems at shore base installations could be fitted with ion exchange chromate removal equipment, for example. This might also be possible on shipboard for radar cooling and marine diesel cooling systems. Facilities where relatively small quantities of chromate

waters need be depolluted on a noncontinuous basis, e.g., maintenance garages for cars and trucks, could be equipped with "chromate destroyers" (small automated systems for destruction of chromates by chemical reduction-precipitation) originally developed for small plating plant operations. These are commercially available and in the smallest sizes require only 2 to 3 square yards floor space. Plumbing and electrical requirements are minimal. Small units of this type could also be mounted on trailers and thus made mobile for basewide or shipwide use.

All modes of chromate removal involve extra complexity and usually expense, however, and there are also Navy practices, e.g., the high-rate discharge of chromate-inhibited ballast tank water, where none of the methods described would be effective. In these instances, a nonchromate inhibitor is highly desirable. Many water treatment companies offer nonchromate inhibitors (64, 65). They are generally not as effective as straight chromates or the low-chromate formulations which have been developed over the years (66). (The low-chromate inhibitors are usually chromate-phosphate-zinc-organic blends. Their chromate content is in the range 20 to 50 ppm, appreciably lower than the 300 to 500 ppm required in the same system when chromate alone is used. However, while they reduce possible chromate pollution, they add zinc and phosphates, pollutants themselves, especially zinc (67).) In particular, nonchromate inhibitors are not able to protect as wide a variety of metals, either singularly or in galvanic contact, as chromate inhibitors. In systems constructed of one metal, or two or more compatible metals, they may work very well. A nitrite-borate mixture was recommended, for example, for trial as a substitute for sodium chromate in locked-in ballast tanks (essentially all low-carbon mild steel) following evaluation of nonchromate inhibitors at the Naval Ship Engineering Center, Philadelphia (65).

The number of nontoxic corrosion inhibitors is few, and the range of metals and conditions with which they are effective is limited. Nonetheless, it is clearly in the public interest that the Navy should endeavor to employ nontoxic inhibitors in every circumstance where the applied inhibitor cannot be scrupulously excluded from the environment. Innovative and developmental studies to increase our store of nontoxic inhibitors or to extend the scope of those presently available should likewise be a matter of Navy concern.

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ANALYSIS There has been concern recently of the possibility of long-term disturbances of our environmental ecology by hexavalent chromium discharged in industrial and, in some cases, naval waste waters. To aid in the assessment of these potential dangers, the literature was surveyed to provide a perspective overview of the toxicities of hexavalent chromium toward plant and animal. The means available for reducing chromate concentrations in waste waters to ppm levels were reviewed for suitability for Navy usage. The techniques considered were chemical reduction, with subsequent precipitation of the trivalent chromium product; ion exchange; direct precipitation; ion flotation; electrochemical reduction; and electrodialysis.		
Background and orientational information are furnished for use in considering Navy chromate pollution problems and their rectification.		

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